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CARNEGIE INSTITUTE OF TECHNOLOGY
METALS RESEARCH LABORATORY

RESEARCH REPORT



Progress Report

Contract N6ori-47/IV Project NR 031-014

SULFUR PRESSURE MEASUREMENTS OF MOLYBDENUM SESQUISULFIDE
IN EQUILIBRIUM WITH MOLYBDENUM

by

C. Law McCabe

PITTSBURGH, PENNSYLVANIA, DATE January 15, 1954

TABLE I. Summary of Experimental Data

Run Number	Orifice area cm	Duration of run, minutes	T	Weight loss of cell, grams
3	0.01497	955	1423	0.0300
6	0.00693	1182	1423	0.0176
7	0.00693	978	1425	0.0154
11	0.01497	5603	1327	0.0166
13	0.00693	6820	1377	0.0362
18	0.00693	2530	1397	0.0200
19	0.00693	2475	1397	0.0185
26	0.00777	2455	1393	0.0207
27	0.00777	2631	1395	0.0250
28	0.00777	2550	1393	0.0238
29	0.00777	4035	1351	0.0139
30	0.01497	5558	1303	0.0095
31	0.01497	3950	1327	0.0111
32	0.01497	3903	1327	0.0120

TABLE II. Summary of Experimental Data

Run Number	Pressure of S ₂ in atmospheres	Log of P _{S₂}	T	1/Tx10 ⁴
3	1.77x10 ⁻⁶	-5.752	1423	7.027
6	1.88x10 ⁻⁶	-5.737	1423	7.027
7	1.94x10 ⁻⁶	-5.712	1425	7.018
11	1.38x10 ⁻⁷	-6.860	1327	7.536
13	6.12x10 ⁻⁷	-6.213	1377	7.262
18	9.19x10 ⁻⁷	-6.037	1397	7.158
19	8.51x10 ⁻⁷	-6.070	1297	7.158
26	8.81x10 ⁻⁷	-6.055	1393	7.179
27	1.02x10 ⁻⁶	-5.990	1395	7.168
28	1.01x10 ⁻⁶	-5.995	1393	7.179
29	3.50x10 ⁻⁷	-6.456	1351	7.402
30	7.77x10 ⁻⁸	-7.110	1303	7.675
31	1.32x10 ⁻⁷	-6.879	1327	7.536
32	1.45x10 ⁻⁷	-6.839	1327	7.536



Figure I.

- A Debye-Scherrer patterns of Molybdenite as received.
- B Pattern of the residue after equilibrium established between sulfur vapor, molybdenum, and the sulfide. The lines marked are those of molybdenum.
- C Pattern after molybdenum metal was dissolved from sample whose pattern is shown in B.

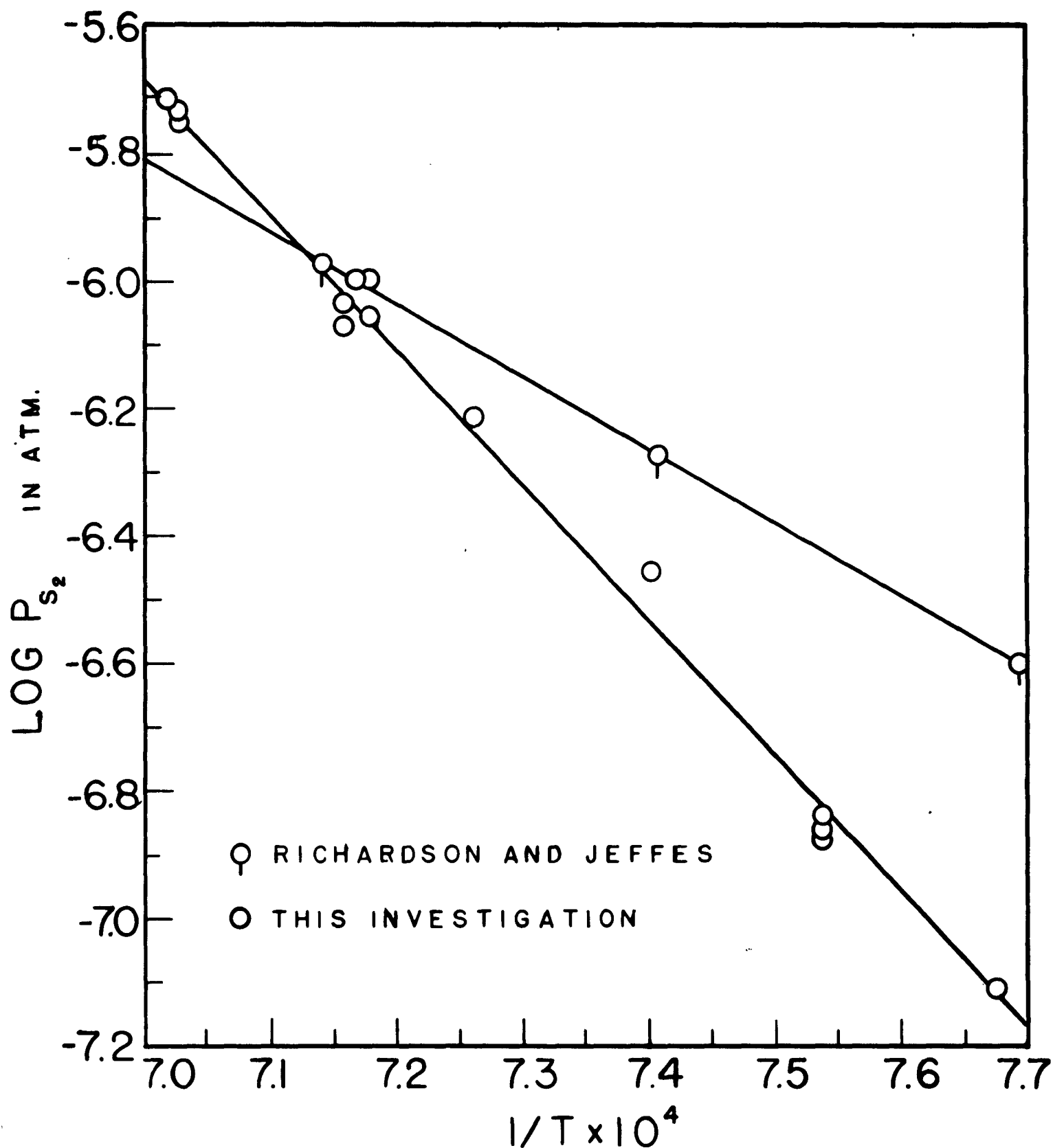


Figure 2. A comparison of the P_{S_2} calculated from data reported here for the reaction $\frac{2}{3} \text{Mo} + \text{S}_2 \rightleftharpoons \frac{2}{3} \text{Mo}_2\text{S}_3$ and that reported by Richardson and Jeffes⁴.

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C. Law McCabe*

Abstract

It has been established that molybdenum sesquisulfide is the sulfide of molybdenum which is in equilibrium with the metal and sulfur vapor in the vicinity of 1100°C. The S_2 pressure for this system has been obtained using the Knudsen Orifice Method and the standard free energy for the dissociation of S_2 .

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Introduction

This work was undertaken to help in determining the thermodynamic properties of the molybdenum sulfide which is in equilibrium with metallic molybdenum and sulfur vapor in the temperature range 1025-1150°C. From the results of Montoro¹ and of Parravano and Malquori² one would expect Molybdenite to be in equilibrium with molybdenum metal, while the results of Guichard³ indicate that a lower sulfide must be in equilibrium with the metal. It was thus concluded that the problem warranted reconsideration, especially in view of the suspiciously low temperature independent term for the standard free energy function for the reaction $\text{MoS}_2 \rightleftharpoons \text{Mo} + \text{S}_2$ which was calculated and duly noted by Richardson and Jeffes⁴, using the data of Parravano and Malquori².

Experimental Method

The general method used in this investigation is that of the Knudsen Orifice Method for determination of the equilibrium pressures. The apparatus and technique are similar to those described for the determination of the vapor pressure of silver in this laboratory⁵. However, a closed end McDanel tube was used to maintain the vacuum instead of fused silica, a molybdenum effusion cell with a replaceable lid was employed instead of a silica cell, and a titanium getter, maintained at run temperature,

was used to assure that no oxidation of the molybdenum or molybdenum sulfide was taking place. All runs were made at a residual pressure less than 10^{-5} mm Hg. The data are given in Table I. Runs 1-13 were obtained using Molybdenite from the Molybdenum Corporation of America. The remaining runs were done with a similar sample from the Climax Molybdenum Corporation.

The weight loss of the cell during heating up and cooling down was subtracted from the total weight loss of the cell during the run. Also, when the temperature was changed, the Knudsen cell was placed in the vacuum chamber and heated at temperature for several hours in order to allow the sulfide and the metal to adjust their compositions to the equilibrium values, to desorb or adsorb gases into or from the molybdenum cell itself, and to desorb any water from the molybdenum sulfide or molybdenum powder inside the cell. Water may have been adsorbed inside the cell because after each run the top of the cell was removed and the material in the cell was stirred to insure that a layer of molybdenum metal would not build up and obstruct the passage of sulfur vapor into the gas phase. It was established that the molybdenum cell alone decreased in weight an inappreciable amount when heated at the highest run temperature for long periods of time.

There are two questions to be answered before the data in Table I can be used to calculate thermodynamic functions. The first is which molybdenum sulfide is in equilibrium with molybdenum metal and sulfur vapor; the second is what sulfur species are present in the vapor phase. One can safely assume that no molybdenum is vaporized since its vapor pressure is negligibly small at these temperatures. It is shown below

that no sulfide of molybdenum is volatile.

Question 1 was answered in the following way. Especially purified Molybdenite from the Molybdenum Corporation of America or from the Climax Molybdenum Company was charged in the molybdenum effusion cell. Debeye-Scherrer patterns of the two original samples were identical. Subsequent experiments on each sample gave identical pressures. Several runs were required to obtain constant weight losses per unit time. After several additional runs were made, the material in the cell was removed and a powder pattern was run. Figure 1 contains the X-ray patterns described below. Molybdenum lines, see pattern B, were very strong and, in addition, weak lines, not those of Molybdenite, were visible. The molybdenum was dissolved out of the sample with dilute aqua regia, and a Debeye-Scherrer pattern and a chemical analysis of the material which did not dissolve was obtained. The Debeye-Scherrer pattern, see pattern C, was totally different from that of Molybdenite and the chemical analysis was 66.0% Mo and 32.0% S. Using elementary methods this corresponds to the chemical formula $\text{Mo}_{2.06}\text{S}_3$. Whether this apparent non-stoichiometry is real or not is problematical, but it is certain that the molybdenum sulfide in equilibrium with sulfur vapor and molybdenum vapor from 1025-1150°C is molybdenum sesquisulfide, Mo_2S_3 .

The second question to be answered, that of the constitution of the sulfur vapor, can only be estimated with fair accuracy at the present time because of the uncertainty of the heat of dissociation of sulfur⁴. Incidentally, a value for this heat of dissociation can be obtained when good gas equilibria data are available for the reaction $\text{Mo}_2\text{S}_3 + 3\text{H}_2 \rightleftharpoons 2\text{Mo} + 3\text{H}_2\text{S}$. This data and the Knudsen data reported here will allow the

calculation to be made. A paper on this method will be forthcoming from work in progress in this laboratory on effusion measurements of iron sulfide in equilibrium with iron. For the present, we will take the value selected by Richardson and Jeffes⁴ for the equilibrium constant for the reaction

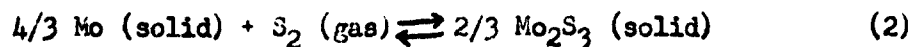


From the data reported by Richardson and Jeffes⁴ it can be shown that no sulfur species other than S_2 and S will be present in appreciable concentration in the gas phase.

One further point to be cleared up is to determine if a molybdenum sulfide is volatile or not. To establish this a 0.5002 gram sample of molybdenite containing 59.2% Mo was placed in an open zircon crucible and placed in a vacuum at 1150°C for two days. It was found that there were 0.3333 grams of material left in the cell and it analyzed 86.9% Mo. Thus 97.8% of the Molybdenum was still in the cell. In view of the uncertainty of quantitative removal of the material from the cell, errors in analysis, and other possible losses, we conclude these data show no volatilization of MoS_2 or Mo_2S_3 . Thus, the entire weight loss of the cell during the effusion runs was due to loss of sulfur.

Calculations

In order to set up the standard free energy for the reaction



it is necessary to obtain the partial pressure of S_2 from the effusion measurements and the equilibrium constant for reaction (1).

On the reasonable assumptions that equilibrium between S_2 and S is maintained in the gas phase, that S_2 and S effuse independently and without interaction, and that ideal gas behavior is obeyed, the following equation is easily derived from the fundamental Knudsen cell equation⁵.

$$M_{S_2}^{1/2} p_{S_2} + K M_S^{1/2} p_{S_2}^{1/2} - \frac{W.L.}{A} = 0 \quad (3)$$

The symbols are identified as follows:

p_{S_2} is the pressure of S_2 in the gas phase in atmospheres.

M is the molecular weight of the species in question.

W.L. is the weight loss of the cell per minute, in grams.

A is equal to 2658 times the area of the orifice in sq.cm. times the duration of the run in minutes divided by the square root of the absolute temperature.

K is the equilibrium constant for reaction (1).

Using equation (3) the pressure of S_2 has been calculated for the data given in Table I and these values have been listed in Table II. The data in Table II have been plotted in Figure 2. The best line selected for this data is

$$\log p_{S_2} = \frac{-21,200}{T} + 9.13 \quad (4)$$

Unfortunately the entropy data needed to perform other Thermodynamic ^{not} calculations are/available. However, the standard free energy for reaction (2) can be calculated and is

$$\Delta F^\circ = 96,800 + 41.8T \quad (5)$$

This equation is valid in the region 1300-1425°K. Due to the present uncertainty in the standard free energy for reaction (1) the accuracy,

according to the system of Richardson and Jeffes⁴, will be Accuracy C or ± 10 kcal.

Using the nomenclature of C. I. Whitman⁶, the value of L/r for the molybdenum cell used in this investigation is 2.9, $W_B = 1$ since the orifice had knife edges, and f for the largest orifice was 0.011. This gives a value of $K = 0.99$. On the assumption that $\alpha = 1$, the pressure for S_2 reported above should be reduced by 1%. The value for α in this case is unknown, but, in view of the fact that the observed pressures were not a function of orifice size, it is concluded that any correction for $K \neq 1$ and $\alpha \neq 1$ is unwarranted in this case. The correction would be a small fraction of the estimated accuracy.

Discussion

From the results presented above it is obvious that either hydrogen does not reduce MoS_2 directly to molybdenum as reported by Parravano and Malquori² or, if it does, one cannot determine the standard free energy of the reaction $Mo (s) + S_2 (g) \rightleftharpoons MoS_2 (s)$ from gas equilibria measurements. This latter statement is true because, if the presence of hydrogen causes the molybdenite to reduce directly to the metal, instead of to the sesquisulfide, then the hydrogen must dissolve in the solid Mo or MoS_2 or both and thereby change the sulfur potential due to its dissolution. The assumption that this does not happen to a marked degree must be made for gas equilibria data to be valid for measuring sulfur potentials. We prefer to think that the observation that the reduction proceeds from MoS_2 directly to the metal is incorrect.

It is likely that Parravano and Malquori² were studying reaction (2)

and not the reduction of Molybdenite directly to the metal. On this assumption one can compare the results of this investigation with theirs. It is seen from Figure 2 that their data and the data from this study give the same Standard Free Energy in the vicinity of 1400°K. However, the temperature coefficient is vastly different in the two cases. The results reported in this investigation give an entropy which is more consistent with that of reactions of this type. The anomalous nature of the entropy term reported by Parravano and Malquori² was pointed out by Richardson and Jeffes⁴.

When better data are available for the energy of dissociation of S_2 , the data reported in Table I will have to be recalculated so that the values for the pressure of diatomic sulfur listed in Table II will be more nearly the correct ones. The estimated accuracy will also be much improved.

Summary

1. The S_2 pressure above molybdenum sesquisulfide in equilibrium with molybdenum has been measured using the Knudsen Orifice Method, coupled with the standard free energy for the dissociation of S_2 .
2. By chemical analysis and X-ray determinations it has been shown that molybdenum sesquisulfide is the sulfide of molybdenum which is in equilibrium with molybdenum metal and sulfur vapor at temperatures around 1100°C.

Acknowledgments

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